

AD-A255 274



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TECHNICAL REPORT 9117

ABSORPTION OF PROPELLANT VAPORS INTO POLYMER FILMS

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AUGUST 1992

U S ARMY BIOMEDICAL RESEARCH & DEVELOPMENT LABORATORY

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Frederick, MD 21702-5010

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Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for Public Release; distribution unlimited.		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 9117			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION U.S. Army Biomedical R&D Laboratory		6b. OFFICE SYMBOL (If applicable) SGRD-UBG-O	7a. NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State, and ZIP Code) Building 568 Fort Detrick Frederick, MD 21702-5010			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION U.S. Army Biomedical R&D Laboratory		8b. OFFICE SYMBOL (If applicable) SGRD-UBG-O	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) Building 568 Fort Detrick Frederick, MD 21702-5010			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. 61787A	PROJECT NO. A878	TASK NO. CA
11. TITLE (Include Security Classification) Absorption of Propellant Vapors into Polymer Films					
12. PERSONAL AUTHOR(S) Hoke, Steven H.; Buffington, Charles O.					
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM Jan 87 TO Sept 91		14. DATE OF REPORT (Year, Month, Day) 1 August 1992	
15. PAGE COUNT 37					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Absorption, Desorption, DNT, TNT nitrobenzen Polymers FTIR. Methylethyl Ketone		
06	14				
07	03				
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A preliminary study of the absorption and desorption of methylethyl ketone and nitrobenzene on various commercial and laboratory prepared polymer films was performed. The development of film exposure techniques along with the evaluation of the feasibility of using FTIR detection of the absorbed vapors was completed. The techniques were tested with 2,4-dinitrotoluene and 2,4,6-trinitrotoluene. DNT and TNT desorption studies for ethyl cellulose and Tedlar were performed.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Steven H. Hoke, Ph. D.			22b. TELEPHONE (Include Area Code) (301) 619-7231		22c. OFFICE SYMBOL SGRD-UBG-O

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INTRODUCTION

The toxicity of airborne munition vapors and their combustion products are of continuing interest to the United States Army and other military branches. Toxicology studies of various nitro organic munitions have been performed¹⁻⁴ in an attempt to establish correct exposure limits for personnel. Due to the extremely low equilibrium vapor pressure of explosive materials, they are often detected by preconcentration. In this process the vapors are concentrated on a suitable surface which can later be heated to desorb the vapor into a detection device, such as a gas chromatograph, for identification.⁵⁻⁷

The purpose of this research is to evaluate an alternative method for the detection of propellant vapors. This was accomplished by the use of various polymer films as preconcentrators for the vapors. In this study the vapors were detected directly on the films with a fourier transform infrared spectrophotometer (FTIR).

EXPERIMENTAL

Materials

The polymers used in this study were obtained from one of three sources: purchased from a local grocery store, purchased from a chemical supplier, or found in the laboratory or at personal homes. See Appendix B, "Commercial Polymer Data," and Appendix C, "Prepared Polymer Films," for more information on source and thickness. The solvents used were of reagent grade or better. The 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) were recrystallized from munition grade chemicals and were obtained from Aldrich Chemical Company, Milwaukee, WI, and Volunteer Army Ammunition Plant, Tyner, TN, respectively.

Instrumentation

The spectra were collected on a Perkin-Elmer Fourier Transform Infrared Spectrophotometer, Model 1750 that was connected to a Perkin-Elmer 7300 Series Professional Computer equipped with CDS-3 and Search-3 software (Norwalk, CN). The FTIR has a mercury cadmium telluride (MCT) detector and a triglyceride sulfate (TGS) detector with a resolution capability of 0.5 cm^{-1} and 1 cm^{-1} , respectively. The sampling conditions for the various samples are shown in Appendix A.

Exposure Chamber

There were two successful types of exposure chambers developed during this study. The first was a pint Mason-type canning jar in which was placed an accordion-folded piece of stainless steel screen wire to support and separate the sample mounts. Into the jar was placed either up to 10.0 mL of the study solvent or a 10.0 cm diameter piece of filter paper which was impregnated with either DNT or TNT. The filter paper was prepared by first wetting it with 2.0 to 4.0 mL of a methyl alcohol solution of the munition and then allowing the

solvent to evaporate. The film mounts were cut from aluminum sheeting of a size to fit the sample slide in the optical module chamber of the FTIR. There was a 2.0cm diameter hole to allow the beam to penetrate the polymer attached to it. The polymers were attached to the mounts with Scotch Magic tape.

The second type consisted of a 2.7cm diameter by 13.2cm aluminum rod with a 1.2cm diameter hole bored through it (Figure 1). Attached to each end were removable plates to facilitate the placement of the polymer films. This chamber was charged by coating the interior with the study solvent or a methanol solution containing the munition. If a munition was used, the solvent was allowed to evaporate leaving a coating of the dry munition on the walls. The ends of the tube were then covered with munition-coated foil, and the chamber was allowed to approach equilibrium for a minimum of 18 h. The polymer films were then attached and the measurements were begun. The tube vapor chamber was mounted on a V-shaped cell holder with a hose clamp.

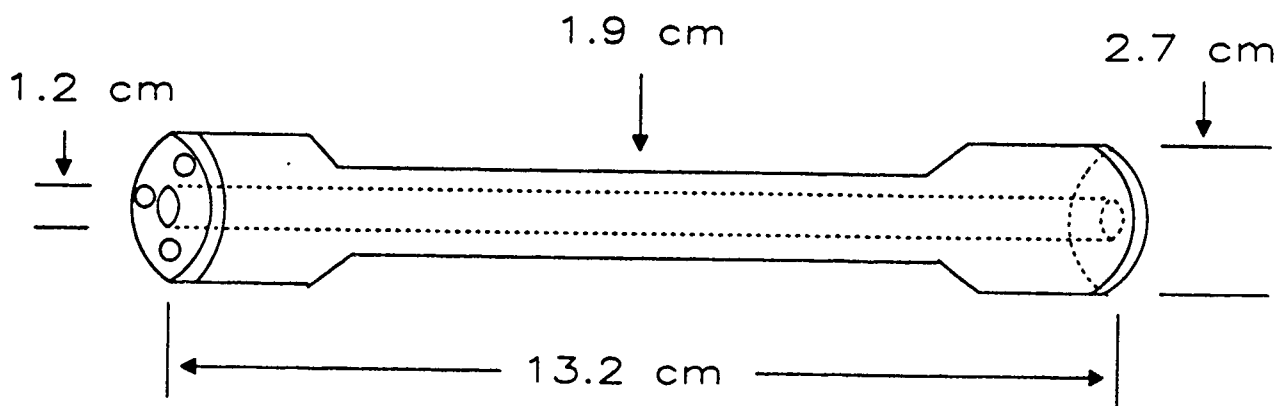


Figure 1. Diagram of the Tube Vapor Chamber

Preparation of Polymer Films

The noncommercial films were prepared from powdered or granular material by dissolving between 0.5 and 1.1 grams of the polymer in approximately 20mL of an appropriate solvent (Table 1). The solvent-polymer mixture was placed in a covered 100mL beaker and stirred in a 40 °C water bath until it dissolved. The amount of the solvent was adjusted to control the thickness of the final film.

The solution was then poured onto a glass plate and placed in the hood to evaporate the majority of the solvent. The glass plate with the partially hardened film was then placed in a vacuum oven, 21 in of Hg below atmosphere at 80 °C, overnight to remove any residual solvent. The poly(methylacrylate) needed several days in the oven to become a somewhat stable film.

Table 1. Polymer - Solvent Combination

Polymer	Solvent	Mass Used (g)
Cellulose triacetate	Dichloromethane	1.0
Ethyl cellulose	Lacquer thinner	1.0
Poly(acrylonitrile)	Dimethylformamide	0.63
Polycarbonate resin	Dichloromethane	1.0
Poly(methyl acrylate)	Acetone	0.63
Polystyrene	Methylethyl ketone	1.0
Polyvinyl chloride High molecular weight	Chlorobenzene	0.55
Polyvinyl chloride Low molecular weight	Chlorobenzene	0.55
Poly(vinylidene fluoride)	Methylethyl ketone	0.63

RESULTS

Comparison of the Two Vapor Chambers

The jar vapor chamber allowed the exposure of up to seven film samples simultaneously to either the study solvent or to the munition. The volatile solvent could be placed directly in the bottom of the jar, and the sample mount could be supported and separated by the screen wire support. An unsuccessful attempt at exposing the polymers to DNT was to place approximately 1.0 g loosely in the bottom of the jar. No detectable DNT absorption could be found after a period of 330 h. To improve the surface area and, therefore, the vapor concentration of the munition, the impregnated filter paper sheets were used. This produced acceptable time limits for the development of absorption spectra.

The tube vapor chamber was developed in hope of being able to observe the absorption of the vapors in the polymers in a much faster time frame and to eliminate the deficiencies with the jar chamber. In the jar chamber, the film mounts would adsorb the vapors as well as the polymers, and the surface area of the film was only 12.2 percent of the mount. The film mounts having a large exposed area of oxidized aluminum did have an effect since it was found that aluminum oxide is a good adsorber for DNT and TNT.⁸ The interior walls of the jar were probably adsorbing the vapors also. This was not a problem with the highly volatile solvents, but with the munition this did affect the

rate of absorption into the polymer films.

The tube vapor chamber's interior was entirely covered with the volatilizing substance so that the only surface that could adsorb the vapors was the polymer films. The disadvantages of the tube chambers are that a different chamber was needed for each film studied and that the vapors were able to evaporate through the films in at least one case. It was observed that the calculated area of the C=O peak actually decreased with time for methylethyl ketone (MEK) in ethyl cellulose (EC); and when the tube vapor chamber was opened at the end of the experiment, there was no odor of MEK.

Absorption of Methylethyl Ketone

Methylethyl ketone (2-butanone) was selected for the initial study of the absorptive properties of a selection of readily available polymer films. The commercial films consisted of a mixture of wraps and bags purchased at a local grocery store. These samples were augmented with polymers found at other sources. The films were mounted on pieces of mat board and placed in a jar vapor chamber. The FTIR spectra were run for Glad Cling Wrap at various intervals for the next 16 h. The other films were checked at the end of this period. The absorption of the ketone was confirmed by the appearance of a carbonyl peak in the 1780 to 1700 cm^{-1} region of the spectrum and by using the "Area" function of the CDS-3 software.

The mat board was used as an initial film mount, but it was found that it was a major absorber of the MEK vapors. It then released the vapors in the optical module chamber of the FTIR producing incorrect spectra. The mat board mounts were replaced with aluminum mounts for the remainder of the study.

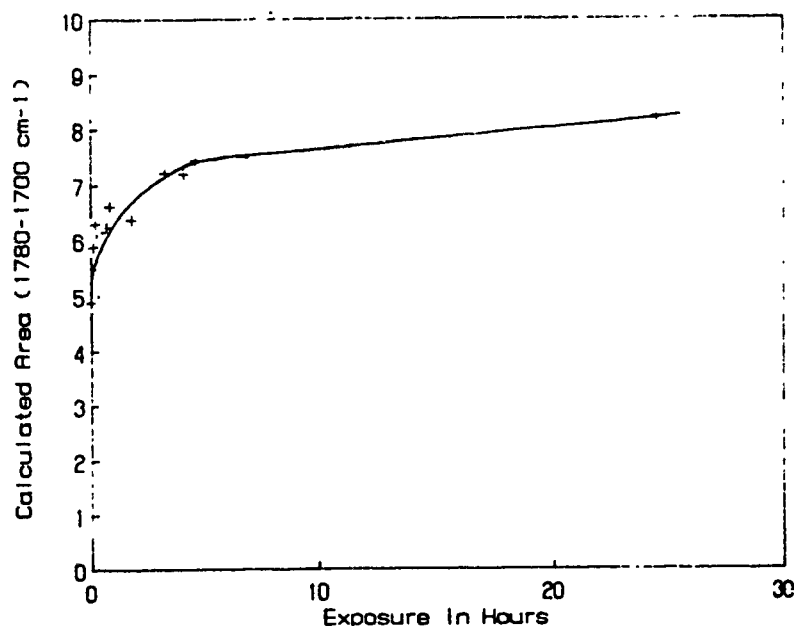


Figure 2. Absorption of Methylethyl Ketone in Glad Cling Wrap

It can be seen in Figure 2 that the amount of absorbed ketone in the Glad Cling Wrap approaches a plateau after approximately 3 h. The presence of MEK in all films was evident as seen from the increase in the calculated areas shown in Table 2.

Table 2. Relative Calculated Area of the Carbonyl Peak for Various Polymers Exposed to Methyl ethyl Ketone

Polymer Film	Unexposed Area	Exposed Area (16 h)
Copolymer A	2.79	9.11
Glad Cling Wrap	2.16	4.27
Glad Sandwich Bag	1.91	4.40
Saran Wrap	5.51	31.51
Scotch Magic Tape	5.51	192.51
Teflon Cap Liner	14.87	19.67

Desorption of Methyl ethyl Ketone

After the films had been exposed to the MEK in the jar vapor chamber for approximately 25 h, a desorption study was performed. This was done by removing a film from the chamber and exposing it to the room atmosphere. The FTIR spectra were taken at approximately 2 min intervals to monitor the disappearance of the MEK from the film. A sample of the spectra showing the desorption of MEK from Glad Cling Wrap is shown in Figure 3. As can be seen from Table 3, most of the films showed no retention after 14 min. Saran Wrap showed slightly longer retentions. The main exception was the Tedlar (TED) sample bag that still had 10.9 percent retention, calculated from the peak area, at 27.5 h. The detection of the presence of MEK vapors in the optical module chamber was the reason to use a new background after every two scans. The vapors were believed to be off-gassing from the mat board mounts.

Absorption of Nitrobenzene in Various Commercial Films

Two jar vapor chambers were prepared, each containing 2 mL of nitrobenzene. The films were attached to aluminum film holders and placed in the jar vapor chambers after the reference spectra were taken. The FTIR spectra were obtained at various intervals over the next several days.

All of the spectra showed some absorption of nitrobenzene. The N-O stretch absorption was most evident in the range of 1542 to 1506 cm^{-1} . Table 4 shows the CDS calculated areas for the 1542 to 1506 cm^{-1} portion of the spectrum for the various films after exposure to nitrobenzene.

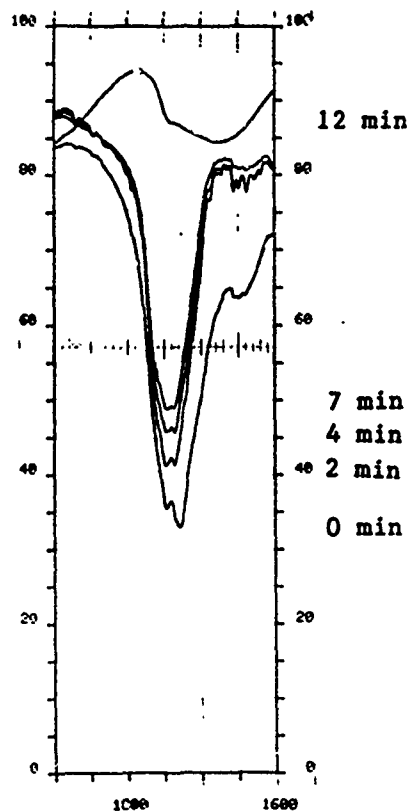


Figure 3. Desorption of Methylethyl Ketone from Glad Cling Wrap

Table 3. Desorption of Methylethyl Ketone from Various Films

Polymer	Time to Baseline
Copolymer A	12 min
Glad Cling Wrap	14 min
Glad Sandwich Bag	14 min
Saran Wrap	32 min
Tedlar Sample Bag	27.5 h*
Teflon	12 min

* C=O peak still visible

Table 4. Nitrobenzene Absorption of Various Commercial Polymer Films

Polymer Films	Area of the 1542 to 1506 cm^{-1} Peak			
	0 h	26 h	69 h	170 h
Copolymer A	6.44	11.07	13.76	15.69
Glad Microwave Wrap	2.72	25.69	40.18	54.13
Glad Storage Bag	7.62	8.18	10.22	12.49
Generic Zip-type Bag	11.55	19.18	23.06	31.22
Large Bag	9.01	19.42	20.99	25.59
Saran Wrap	8.67	29.41	52.48	67.21
Safeway Plastic Wrap	4.78	4.83	4.73	6.57
Safeway Storage Bag (1.75 mils.)	7.43	9.89	11.49	14.98
Tedlar Sample Bag	9.76	15.72	29.08	95.03
Ziplock Freezer Bag (2.7 mils.)	9.88	17.31	20.54	25.93

Figure 4 shows the absorption curve for selected polymer films with nitrobenzene. It can be noted from the curve that all three of the polymers absorb nitrobenzene for the first 145 h. Of the three, TED appears to be the best absorber.

In Figure 5 the reference spectrum for Glad Microwave Wrap and the final absorption spectrum of nitrobenzene in Glad Microwave Wrap are shown. The appearance of the additional peaks due to nitrobenzene can be seen in the second spectrum. The manipulation of this data by the "Difference" software⁹ produced the "Difference" spectrum which made it easy to identify the substance absorbed as nitrobenzene.

Absorption of Nitrobenzene in Prepared Polymer Films

The absorption of nitrobenzene was performed using various prepared polymer films and the jar vapor chambers. All the polymers except poly(acrylonitrile) (PAN) showed significant absorption of nitrobenzene by the termination of the experiment. Ethyl cellulose demonstrated the best absorption, exhibiting obvious nitrobenzene peaks after 3 h. The absorption, by calculated areas, for the 1550 to 1490 cm^{-1} region of the films during the experiment is shown in Table 5. The plots of the data can be seen in Figure 6.

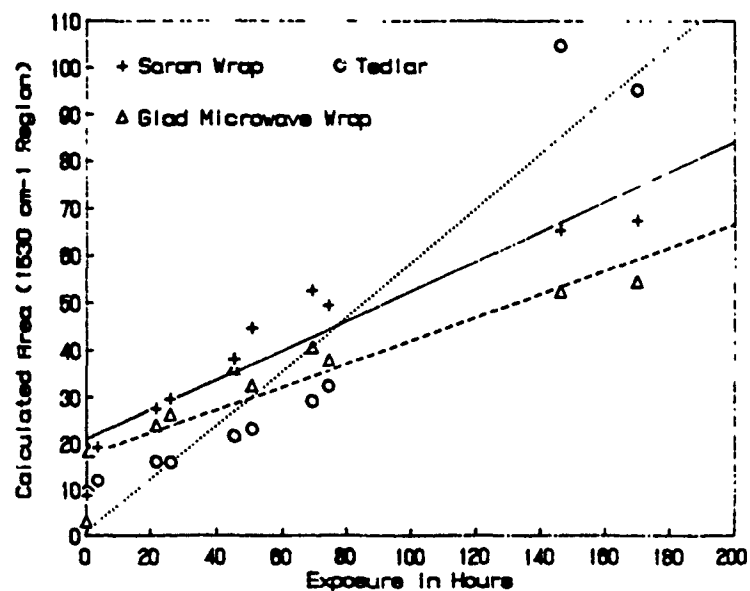


Figure 4. Nitrobenzene Absorption Curves in Three Commercial Polymers

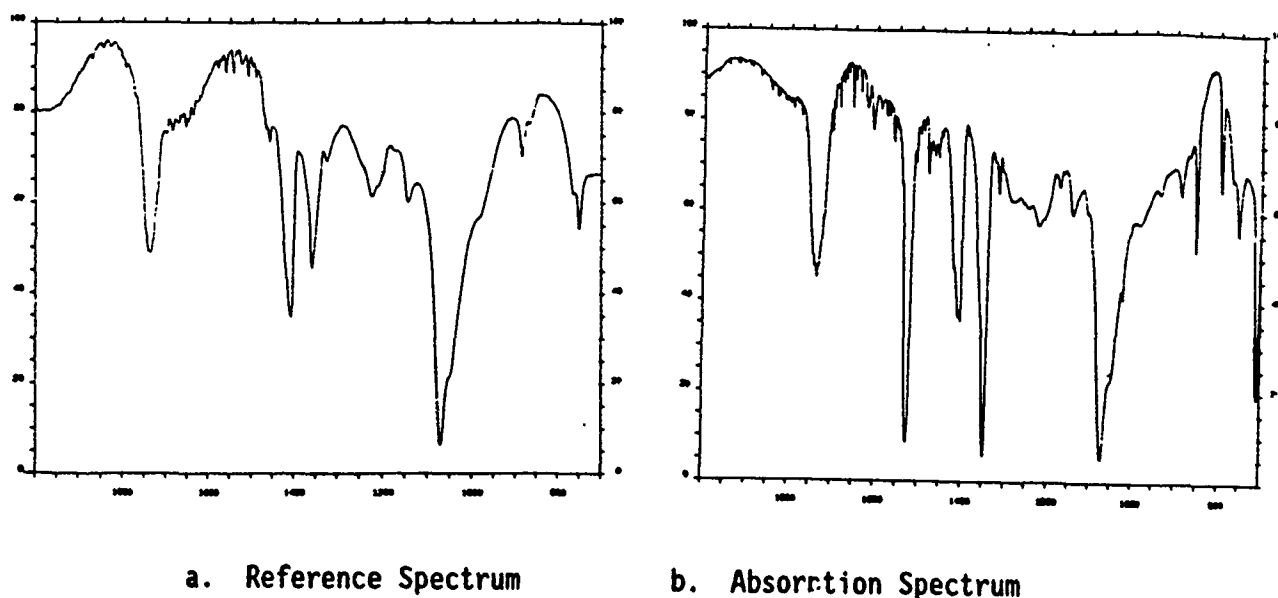


Figure 5. Comparison of the (a) Reference Spectrum of Glad Microwave Wrap to the (b) Absorption Spectrum of Nitrobenzene in Glad Microwave Wrap

Table 5. Absorption of Nitrobenzene in Various Prepared Films

Prepared Peak Polymer Films	Symbol	Calculated Area of the 1,550 to 1,490 cm ⁻¹								
		0.0 h	3.0 h	25.0 h	55.0 h	79.0 h	104.0 h	194.0 h	242.0 h	
Cellulose triacetate	CTA	29.96	68.52	134.85	143.23	144.45	146.44	165.81	171.75	
Ethyl cellulose	EC	19.22	88.29	110.48	144.10	159.75	159.96	158.86	172.39	
Poly(acrylonitrile)	PAN	*	8.37	8.31	9.28	9.44	9.16	8.89	9.55	
Polycarbonate	PC	207.31	211.58	233.79	288.94	324.83	349.01	369.27	346.19	
Polyethylene vinyl acetate	PE-VA	13.78	25.23	29.84	32.83	33.99	36.94	33.31	36.05	
Poly(methylacrylate)	PMA	21.54	21.14	21.53	30.02	40.42	87.13	**	**	
Polystyrene	PS	96.13	97.30	112.43	167.27	212.15	212.74	**	**	
Polyvinyl chloride High molecular weight	PVCH	20.00	19.12	23.15	58.83	123.02	112.78	145.99	151.75	
Polyvinyl chloride Low molecular weight	PVCL	5.27	5.09	10.96	39.59	112.36	116.00	132.94	140.47	
Poly(vinylidene fluoride)	PVF	3.98	6.81	11.01	11.89	12.70	13.61	14.94	18.51	

* Spectra lost in analysis

** Film broke in holder

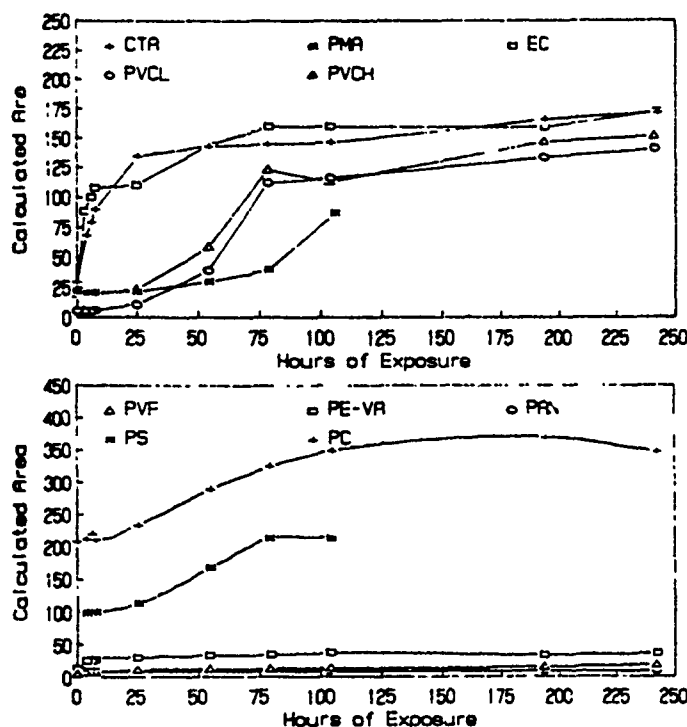


Figure 6. Nitrobenzene Absorption in Various Prepared Polymer Films

The absorption of nitrobenzene was repeated using the tube vapor chamber for two polymers, Tedlar and ethyl cellulose. The nitrobenzene was detected in the films after about 5 min for both films. This included the time needed to assemble the tube and obtain the spectrum. The amount of absorbed nitrobenzene continued to increase for both polymers during the next 3 to 4 h. The ethyl cellulose plateaued after 3 h and the Tedlar plateaued after 4 h. To determine if all the nitrobenzene had been absorbed, more nitrobenzene was added to the Tedlar tube chamber after 31 h. The calculated areas for the NO_2 peak continued to fluctuate around the plateau level. The plot of the data can be seen in Figure 7.

Desorption of Nitrobenzene from Commercial Films

To test the desorption of nitrobenzene, the two films which had absorbed the most were selected, copolymer A and Glad Microwave Wrap. The film was removed from the jar vapor chamber, and a spectrum was immediately taken. The film mounts and the polymers were placed in a rack and left exposed to the laboratory atmosphere. Spectra were taken every 2 min for the next 1/2 hour and several times thereafter. It can be seen from the graphs in Figure 8 that most of the nitrobenzene escaped from the copolymer A within the first 4 min with little decrease over the rest of the time. The Glad Microwave Wrap took slightly more than 2 h for a majority of the nitrobenzene to escape, yet it was still detectable in the spectrum after 48 days. The plots of the data are shown in Figure 9.

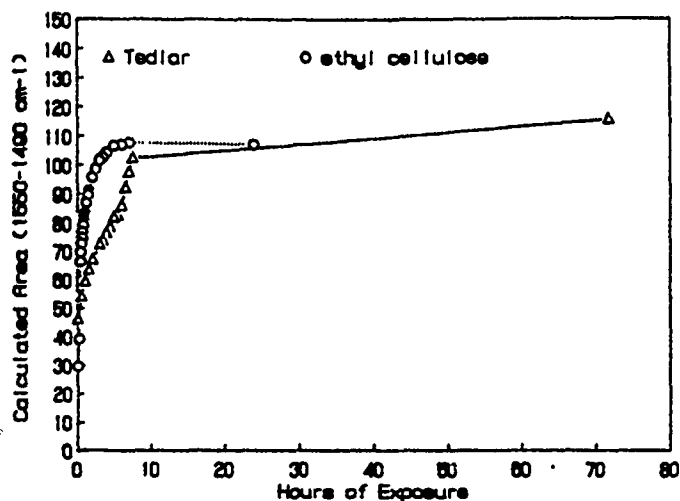


Figure 7. Absorption of Nitrobenzene in Ethyl Cellulose and Tedlar Using the Tube Vapor Chamber

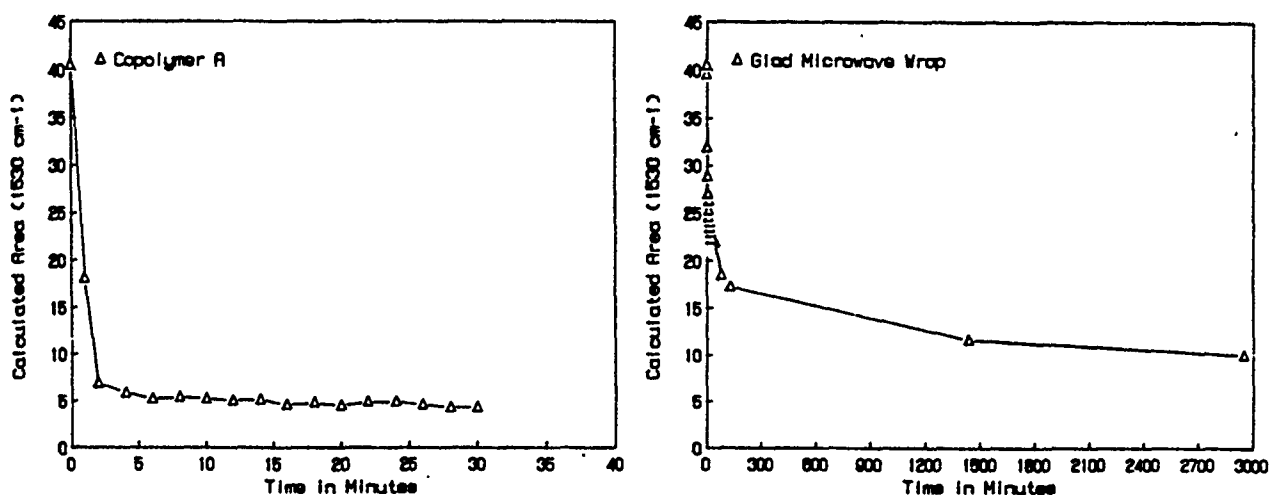


Figure 8. Desorption Curves of Nitrobenzene from (a) Copolymer A and (b) Glad Microwave Wrap

Absorption of 2,4-Dinitrotoluene in Various Commercial Polymer Films

Jar vapor chambers were prepared containing DNT impregnated filter paper and up to six commercial film samples per chamber. The FTIR spectra were obtained at various intervals for a period of 1 wk. Observable DNT peaks could be seen superimposed on the spectra of 11 of the polymers. The base spectrum of Glad Microwave Wrap with the superimposed DNT exposed spectrum is shown in Figure 9. The strong peak at approximately 1530 cm^{-1} is the

first to appear followed by the peaks at about 1608 and 1350 cm^{-1} . The polymers exhibiting absorption in the 1530 to 1540 cm^{-1} region were cellulose triacetate, Ethyl cellulose, Glad Micro Wrap, poly (methyl acrylate), Saran Wrap, Ziplock Freezer Bag, and Ziplock bag B. The polymers that indicated absorption only by an increase in the calculated area for the 130 to 1540 cm^{-1} region were copolymer A, large bag, and Tedlar. The films that did not show any significant change in their spectra or absorption calculations were Glad Storage Bag, polycarbonate, polystyrene, Safeway Cling Wrap, and Safeway Plastic Wrap.

In Figure 10 the "Difference" spectrum calculated by the CDS-3 software and the reference spectrum of DNT are shown. The "Difference" spectrum was calculated for the overlapped spectra shown in Figure 9. By comparing the two spectra in Figure 10, it is easy to identify the substance absorbed in the software produced "Difference" spectrum as DNT.

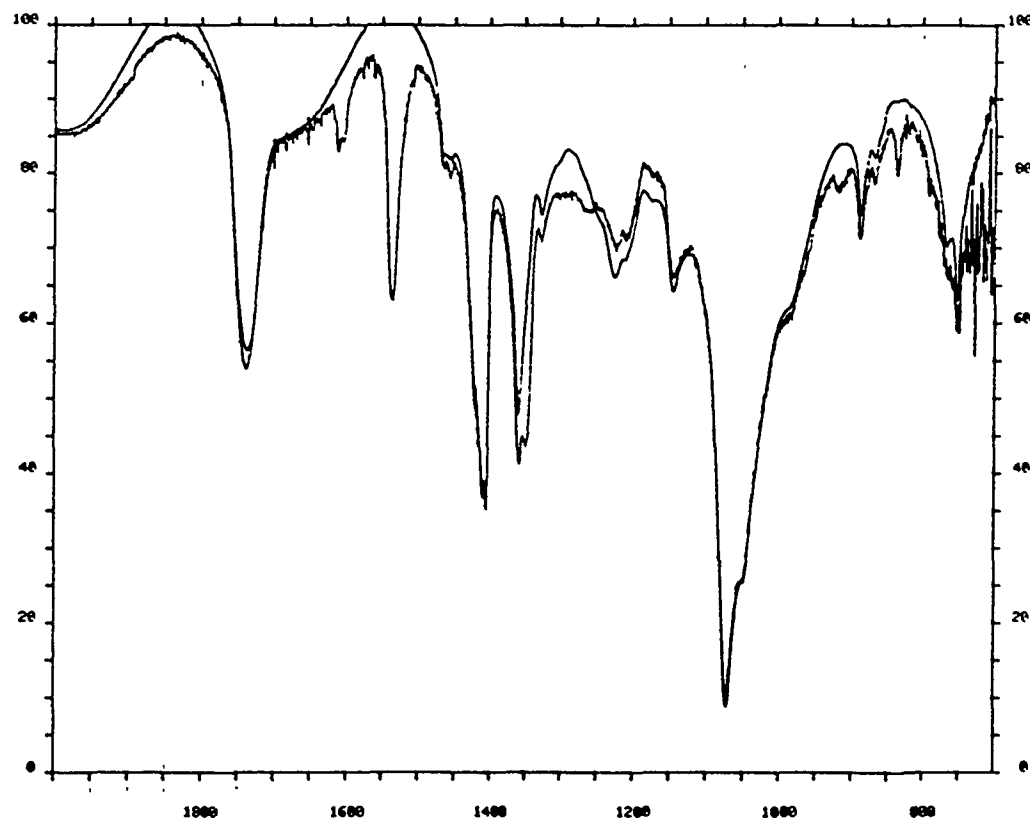


Figure 9. Overlapped Base and Dinitrotoluene Absorption Spectra for Glad Microwave Wrap

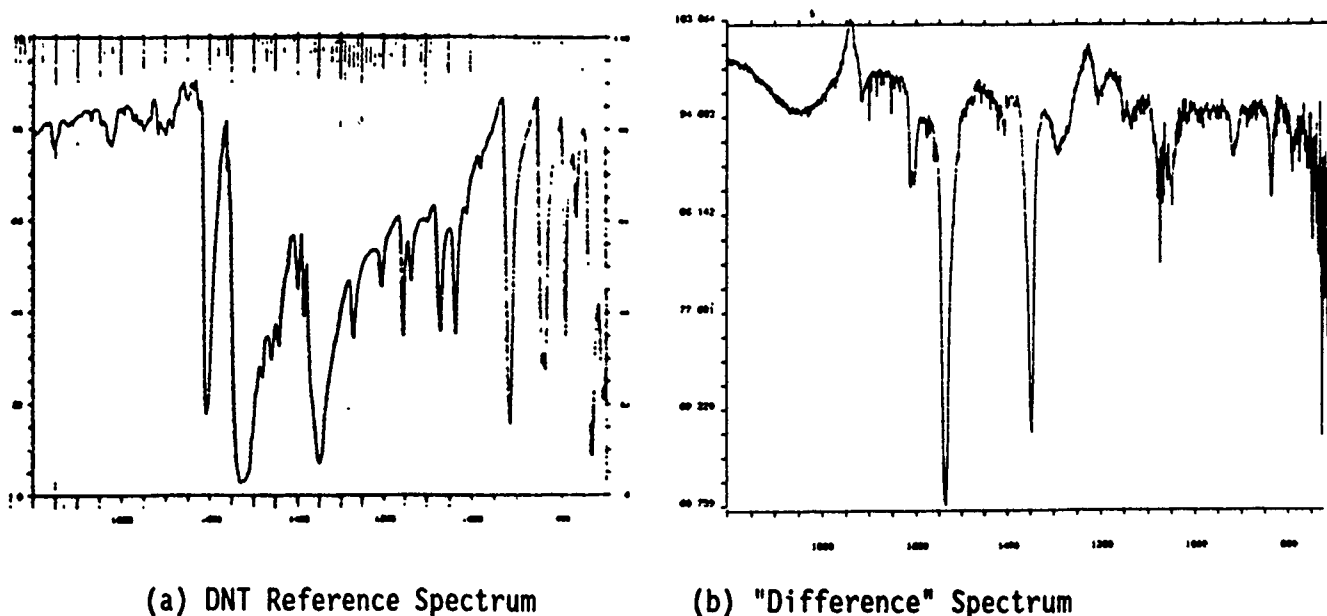


Figure 10. Comparison of the (a) Absorption Spectra of 2,4-Dinitrotoluene to the (b) Calculated "Difference" Spectra

The films were allowed to remain in the chamber for a period of approximately 11 months. At this time spectra were run, and it was observed that a large amount of DNT had absorbed into ethyl cellulose and Tedlar. At the end of 12 months the Tedlar was still showing an increase in absorption. The 12-month spectra for these two compounds are shown in Figure 11.

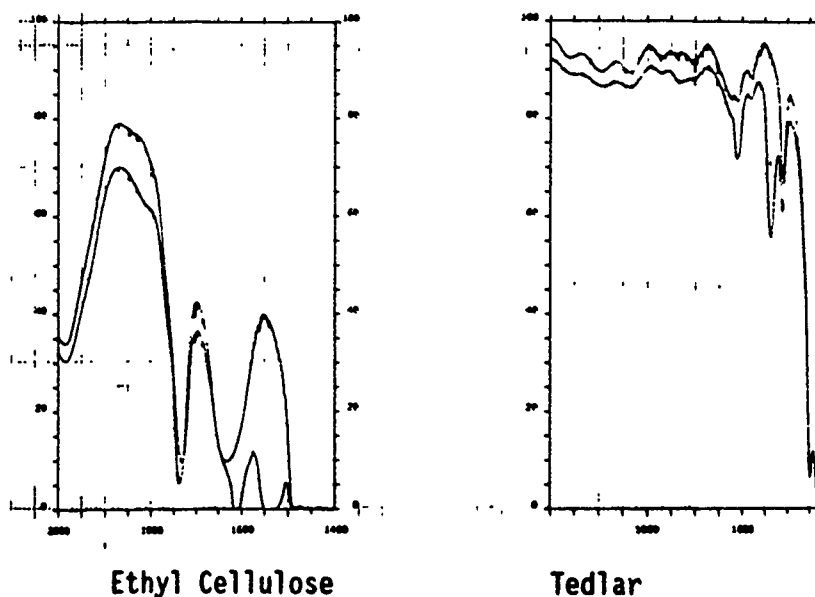


Figure 11. Twelve-Month Dinitrotoluene Spectra for Commercial Ethyl Cellulose and Tedlar Using the Jar Vapor Chamber

Absorption of 2,4-Dinitrotoluene in Prepared Polymer Films

Two vapor jar chambers were prepared, each containing a set of six films, and FTIR spectra were taken at various intervals for 27 days. There were seven different polymers used with different thickness for several of the films. Initially, only poly(vinylidene fluoride) (PVF), Tedlar (TED), and ethyl cellulose (EC) showed any absorption. Polyvinyl chloride, low molecular weight (PVCL); polyvinyl chloride, high molecular weight (PVCH); poly(acrylonitrile) (PAN); and poly (methyl acrylate) (PMA) showed no absorption after 3 wk. There seemed to be no consistent effect due to thickness; the thicker of the two PVF films absorbed better than the thinner while the thinner EC film absorbed more than the thicker. In Table 6 the calculated areas for the 1560 to 1520 cm^{-1} region of selected spectra are given. The increase in the calculated area shown in the table indicates the absorption of DNT by each polymer. In Figure 12, the 27 day spectra one superimposed on the unexposed spectra for PVF and EC. This clearly illustrates the absorption of the DNT in each of the polymers.

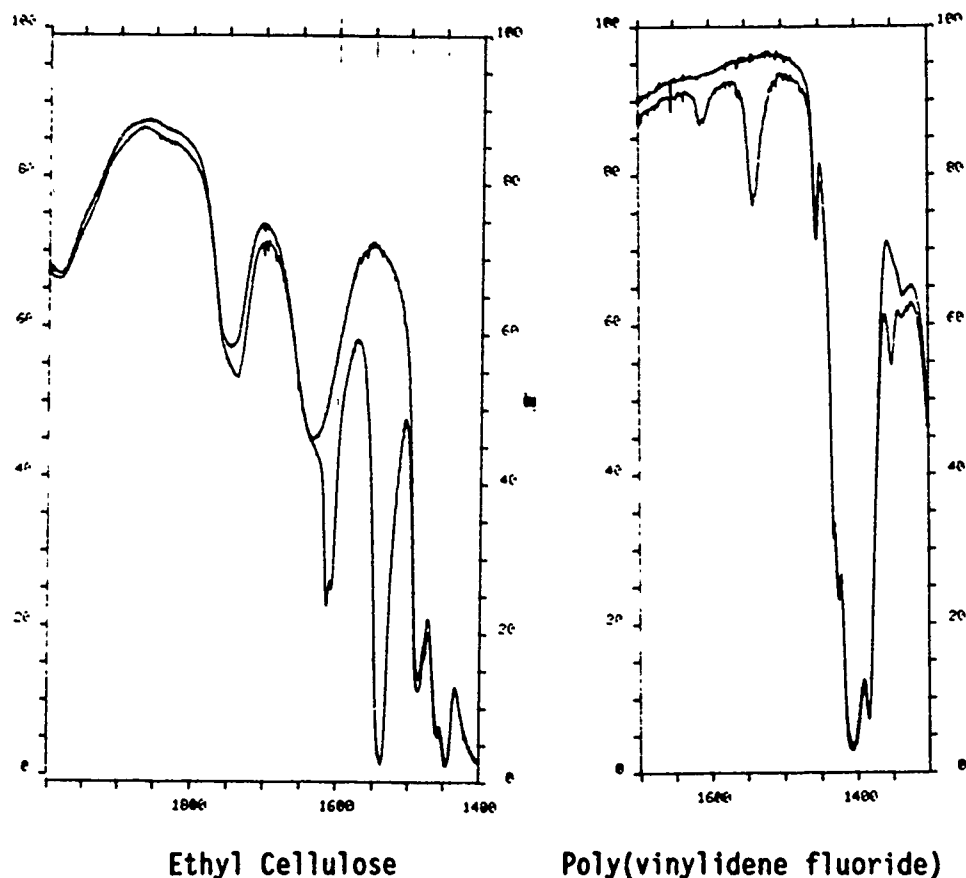


Figure 12. The 27 Day Dinitrotoluene Absorption Spectra of Prepared Poly(vinylidene fluoride) and Ethyl Cellulose Using the Jar Vapor Chamber

Table 6. Absorption of Dinitrotoluene in Selected Prepared Polymer Films

Time (days)	DNT - Area of the 1560-1520 cm^{-1} Region for Prepared Polymers								
	PVCL	PVCH	PVF 1.0 mil	PVF 0.4 mil	TED	PAN	PMA	EC 9.5 mil	EC 2.6 mil
0	3.29	9.21	1.52	2.29	5.23	4.36	9.79	44.00	12.09
1	3.09	9.30	3.18	3.39	14.01	4.62	9.73	45.37	15.48
5	2.98	9.75	4.53	4.20	17.05	4.71	9.73	46.69	26.17
6	2.63	8.99	4.70	3.99	11.50	5.03	9.35	50.43	28.75
7	2.82	8.78	4.33	4.35	6.27	4.56	9.43	52.50	31.40
8	3.13	8.78	5.14	5.04	15.61	4.58	9.60	54.77	34.08
11	2.76	9.22	4.95	4.72	7.87	4.39	9.57	59.87	41.92
12	2.78	8.82	5.34	5.34	8.74	4.62	9.61	61.10	44.21
14	3.21	9.34	5.77	5.29	7.78	4.58	9.36	64.38	48.68
18	2.97	9.44	5.78	5.66	8.70	4.43	9.76	69.92	55.96
22	2.85	9.33	6.60	5.89	8.16	4.41	9.80	78.07	59.72
27	3.20	9.34	5.94	6.19	8.84	4.43	9.79	82.95	65.57

Two polymers, EC and TED, were chosen to repeat the absorption of DNT using the tube vapor chamber. The NO_2 peak was visible on the EC spectrum after 20 to 30 min, while the TED took longer, about 5.5 h. This is obviously faster than the jar chamber which took 24 h for the EC and 55 hour for the TED. Figure 13 shows the tube vapor chamber absorption curves for the absorption of DNT in EC and TED.

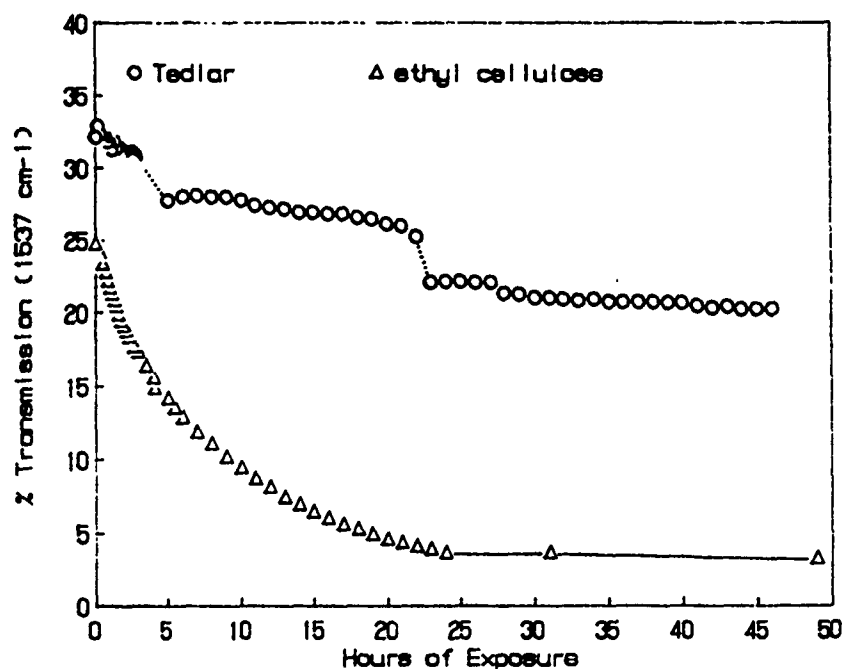


Figure 13. Dinitrotoluene Absorption Curves for Ethyl Cellulose and Tedlar Using the Tube Vapor Chamber

Desorption of DNT from Saran Wrap

A mount containing Saran Wrap, which had been exposed to DNT for more than 2 weeks, was placed in the air and monitored periodically. It can be noted from Table 7 that the rate at which the DNT desorbs from the Saran Wrap was much slower than that of MEK or nitrobenzene, and that after 47 hours there was still 55.5 percent left in the film.

Table 7. Desorption of Dinitrotoluene from Saran Wrap

Time (hours)	Area 1560-1520 cm^{-1}	Percent Remaining
0	12.08	100.0 %
1	11.92	96.8 %
2	11.29	84.3 %
19	10.96	77.7 %
23	10.72	73.0 %
25	10.60	70.6 %
27	9.90	56.7 %
47	9.84	55.9 %

Desorption of DNT from EC and TED

The two films which showed the large DNT absorption after more than 1 yr were removed from the jar chamber and left exposed to the air. The areas for the 1560 to 1520 cm^{-1} for both films, at various intervals, are shown in Table 8. The desorption from TED appeared to be happening at a faster rate than for EC.

Table 8. Desorption of Dinitrotoluene from Ethyl Cellulose and Tedlar

Time (Days)	Ethyl Cellulose		Tedlar	
	Area 1560-1520 cm^{-1}	Percent Remaining	Area 1560-1520 cm^{-1}	Percent Remaining
Unexposed	17.13	.0	2.77	.0
0	157.58	100.0	12.85	100.0
1	150.30	94.8	12.36	95.1
2	160.28	101.9	11.60	87.6
3	144.60	90.8	11.37	85.3
6	151.69	95.8	10.99	81.5
8	156.95	99.6	10.88	80.5
14	143.47	90.0	10.18	73.5
44	123.28	75.6	4.16	13.8
109	90.44	52.2	4.42	16.4
185	66.47	35.1	3.49	7.1
386	47.98	22.0	3.33	5.6

Absorption of TNT in Commercial Polymer Films

Jar vapor chambers were set up with filter paper containing 0.4 g of TNT and a maximum of six films per chamber. A total of 16 films were exposed to the vapors. After 13 days only four films showed any significant increase in the calculated area for the 1560 to 1520 cm^{-1} peak. They were EC, Ziplock Freezer Bag, pretzel bag, and Saran Wrap. When comparing the first and last spectra, only EC showed the start of a discernible peak. The copolymer A showed an enlarging of a broad peak in that region and the Ziplock Freezer Bag appeared to be thickening, since the entire spectrum increased proportionally in absorbance.

Spectra for the films were again run after approximately 11 months, and only EC showed an increase in the amount of TNT absorbed during that time. The spectra obtained after an approximately 1 yr exposure along with the unexposed spectra for EC can be seen in Figure 14.

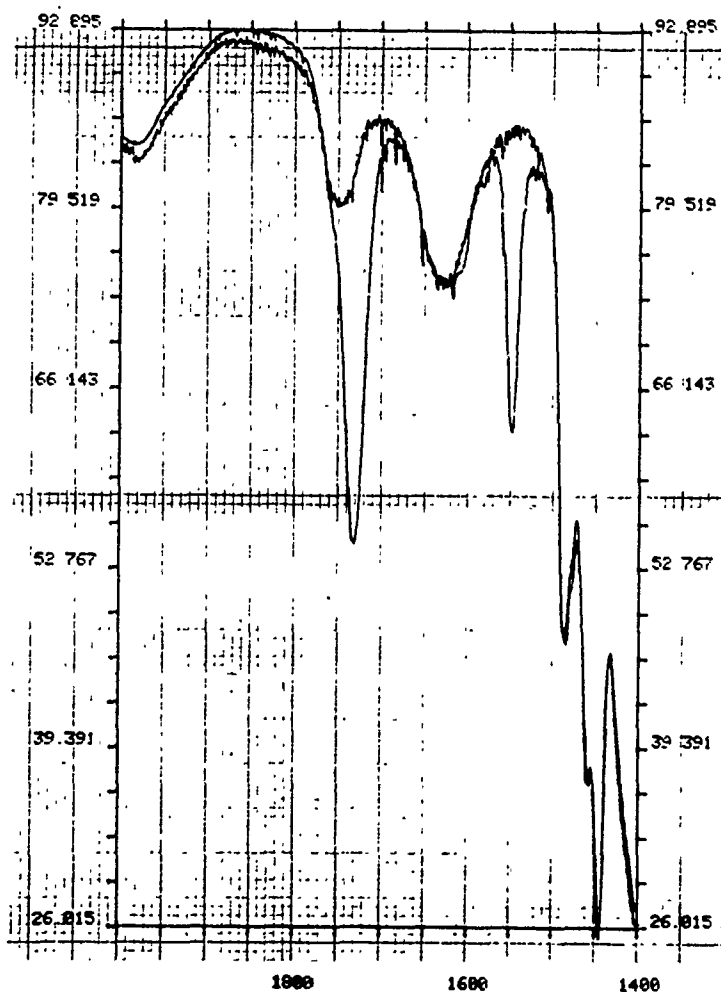


Figure 14. Twelve-Month Absorption of Trinitrotoluene in Commercial Ethyl Cellulose Using the Jar Vapor Chamber

Absorption of TNT in Various Prepared Polymer Films

Twelve different films were divided between two chambers and exposed to TNT vapors. The area calculations from the CDS software (1560 to 1520 cm^{-1} peak) for each film spectrum can be seen in Table 9 and selected spectra in Figure 15. Of the polymers used, only EC showed a significant absorption of the TNT vapors after a period of 13 months. The PVF films showed absorption to a lesser extent for this period. The peaks, caused by the NO_2 absorption, are visible on the superimposed spectra of both EC and PVF in Figure 15. The lesser degree to which PVF absorbed the TNT is evident by the size of the peaks.

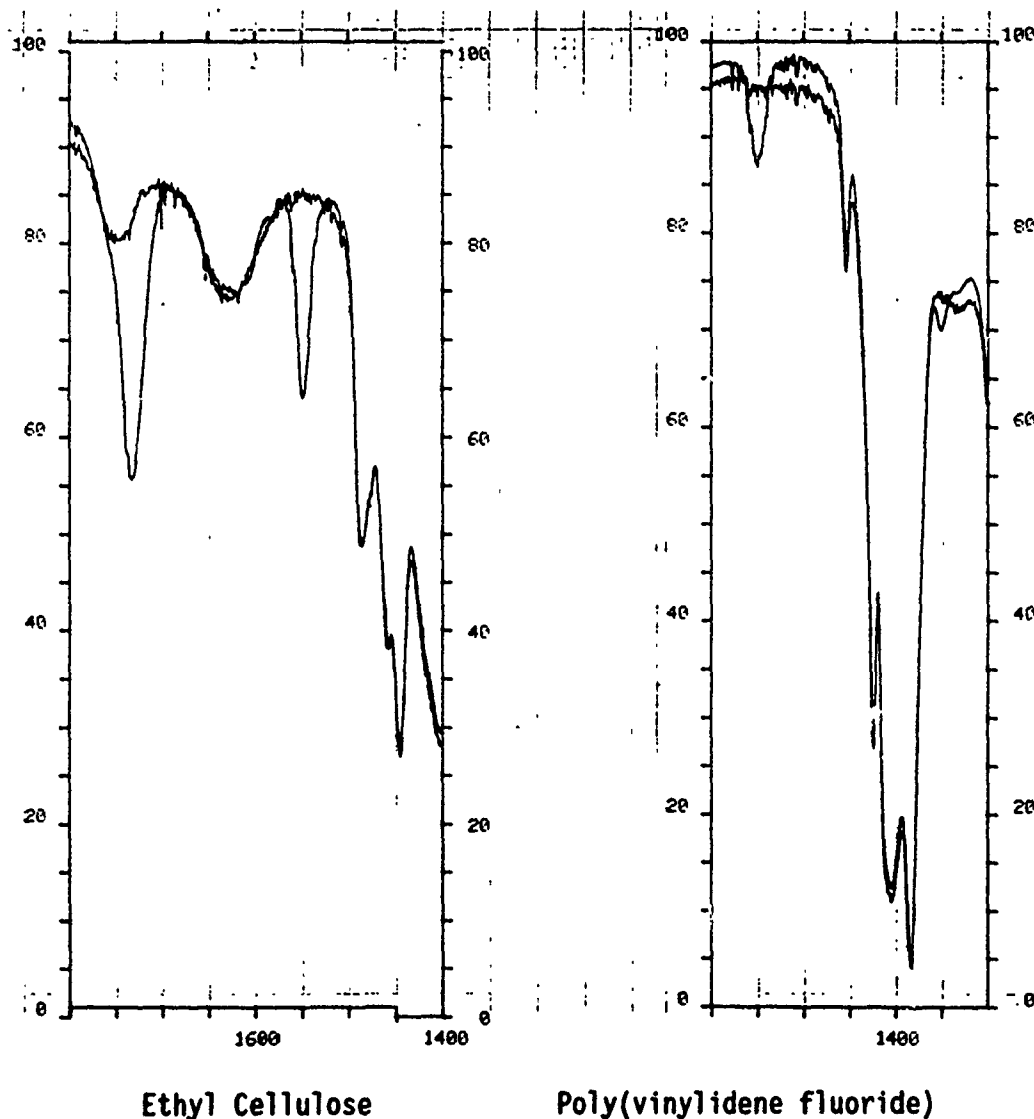


Figure 15. Thirteen-Month Trinitrotoluene Absorption Spectra for Prepared Ethyl Cellulose and Poly(vinylidene fluoride) Using the Jar Vapor Chamber

Table 9. Trinitrotoluene Absorption for Selected Prepared Polymer Films Using the Jar Chamber

Time (days)	TNT - Area of the 1560 to 1520 cm^{-1} Region for Prepared Polymers							
	PVF 0.4 mil	PVF 1.8 mil	PVF 0.2 mil	PVCL	PVCH	PMA	PAN	EC 1.4 mil EC 3.0 mil
0	1.47	6.40	1.67	7.06	12.27	10.49	4.12	5.41 13.77
1	1.41	6.20	1.60	7.11	12.58	10.59	4.29	5.56 14.02
2	1.69	6.47	1.68	6.79	12.31	10.29	4.16	5.54 14.27
3*	1.16	5.16	1.59	6.66	10.76	10.47	4.22	5.89 14.54
4	1.59	5.25	1.59	6.42	10.80	10.32	4.28	6.00 14.58
7	1.55	4.95	1.61	6.63	11.53	10.08	4.38	6.31 14.87
8	1.18	4.40	1.55	6.38	10.68	10.02	4.18	5.92 14.51
9	1.64	5.13	1.41	6.40	10.47	10.23	3.07	6.16 15.23
10	1.63	5.35	1.54	6.52	10.65	10.43	4.39	6.37 15.35
13	2.26	5.58	2.05	6.40	10.50	10.26	4.17	6.34 15.63
14	1.62	5.51	1.59	6.25	10.76	10.07	4.04	6.30 15.69
16	2.47	5.89	1.20	6.49	11.06	10.45	4.20	6.81 15.89
20	2.27	5.89	1.81	6.61	10.97	10.52	4.33	6.91 16.45
24	2.06	6.16	1.66	6.85	10.96	10.48	4.25	7.13 18.82
30	2.52	6.25	1.78	6.45	10.96	10.54	4.22	7.04 17.53

* Instrument underwent maintenance.

The tube vapor chamber was used to expose two films, EC and TED, to TNT. The same effect was noted this time as before; the absorption rate was faster than the jar vapor chamber. With the tube chamber EC showed a visible peak in 2 hours and the TED in 4 hours, whereas the jar chamber showed a peak with EC in 11 days and showed no peak with TED. The clarity of the NO_2 peak on EC from the tube vapor chamber at 11 days compares favorably to the 12 month peak from the jar vapor chamber. This is evident by comparing Figures 14 and 16.

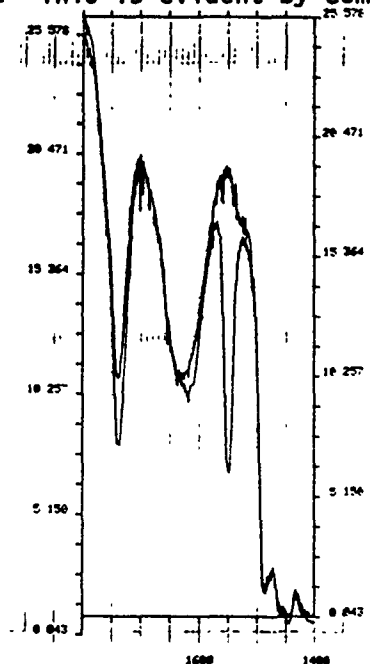


Figure 16. Eleven-Day Spectrum of Trinitrotoluene Over the Reference Spectrum of Ethyl Cellulose Using the Tube Vapor Chamber

Desorption of TNT from Ethyl Cellulose

The EC film which had been exposed to the TNT vapors for 1 yr was removed from the vapor chamber and exposed to air. The FTIR spectra were taken periodically over a period of time to monitor the decrease in the calculated area (CDS software). The TNT was desorbing at a slower rate from the EC than the DNT. The data for the desorption of TNT from EC is given in Table 10.

DISCUSSION

The three DNT FTIR peaks that were observed in this study were assigned as follows: 1608 cm^{-1} - skeletal vibrations within the C-C bonds in the benzene ring; 1530 cm^{-1} - asymmetrical stretch of the N-O bond along with skeletal vibrations of the C-C bonds in the benzene ring; and 1350 cm^{-1} - symmetrical stretching of the N-O bonds.

The rate at which the DNT absorbs, as well as the concentration of the vapors in the atmosphere needed for the polymers to absorb, may limit the practicality of their use as passive detectors in an open-air situation.

Table 10. Desorption of Trinitrotoluene from Ethyl Cellulose

Time (days)	Area	Percent Remaining
Unexposed	16.75	.0
.0	32.82	100.0
0.7	32.82	100.0
0.25	32.82	100.0
1.0	32.69	99.2
1.3	32.78	99.8
2.0	32.47	97.8
3.0	33.18	102.7
6.0	32.14	95.8
8.0	32.14	95.8
9.8	31.99	94.8
41.2	30.77	87.2
109.0	28.72	74.5
185.0	28.75	74.5
386.0	29.03	76.8

This was illustrated by the fact that the best results were obtained when the atmosphere was saturated with vapor, as indicated by the tube vapor chamber producing faster, measurable absorption than did the jar vapor chambers. The fact that aluminum and aluminum oxide are good adsorbers of TNT and DNT may be used to explain some of the difference between the two chambers since the film mounts used with the jar chambers were untreated aluminum, whereas, all of the tube vapor chamber's exposed aluminum interior was coated with TNT or DNT. The concentration of the TNT vapors appeared to be highest with the tube vapor chamber since it was the only chamber in which TED was able to absorb TNT.

The use of a small increase in the calculated area of a peak as the only evidence of absorption was somewhat suspect. The best case reproducibility of the numerical values obtained in the area calculation were in the range of 5 percent with the TGS detector and 1 percent with the MCT detector with six scans. The best reproducibility was obtained with six scans using the MCT detector, 1 cm^{-1} resolution, along with a new background each time. The reproducibility could possibly be increased by using more than six scans, but it was feared, at the time of this portion of the study, that the compound would desorb if left exposed to the air too long. The MCT detector was used because it is faster than the TGS detector, thus allowing more scans in less time. The difficulty with the reproducibility may have been caused by approaching the limits of the instrument or, more likely, by the nonuniform placement of the sample. While the films measured consistently with a micrometer, an inconsistency in the thickness of the commercial films could be observed with the FTIR by moving the sample in the beam. This produced area differences greater than the best case 1-percent range.

The laboratory-produced films, obviously, were not uniform in their thickness. There was some noticeable swelling and deformation of the films due to the absorption of MEK and nitrobenzene. The MCT detector was sensitive to the amount of time that had elapsed since the cooling reservoir was filled with liquid nitrogen. The reproducibility began to decrease after about 3 h from the time of filling.

The TGS detector was used instead of the MCT detector initially because it was more convenient. There were several reasons for this. First, the MCT required the use of liquid nitrogen to cool it, and the chamber needed to be filled at least twice a day. The MCT detector also required the placement of attenuator combs in the beam path to reduce the power to the detector so that the spectra would remain on scale. The final reason, as mentioned before, was that the scan range needed to be narrowed to 2000 to 700 cm^{-1} so that the spectrum data points could be transferred to the available spectral data region in the computer for preservation and analysis. The TGS detector also was used with the tube chamber so that the FTIR could be programmed to take readings overnight or during the weekend. This produced an increase in noise in the spectra which in turn caused fluctuations in the area calculations.

The composition of the film appears to have an effect on the absorption of the vapors.² The good absorbers have a portion of the molecule with atoms exposed that have a large electronegativity. For example, Glad Microwave Wrap, copolymer A, and large bag B appear to contain vinyl acetate which has an exposed electronegative oxygen atom in the carbonyl group. Tedlar contains exposed fluorine atoms in its chain. Some of the other polymers listed as polyethylene also may have traces of vinyl acetate or another copolymer in amounts too small to be evident in their spectra.

The desorption of MEK and nitrobenzene occurred rapidly while the DNT took much longer. Again, this could be attributed to the difference in the number of electronegative components in the molecule. DNT has more nitro groups in the molecule and is able to attract to the polymer film by a mechanism using the nitro group oxygen's lone pair electrons.¹¹ The other possibility would be for the nitro groups to produce positive sites by the inductive effect. The positive sites could then be attracted to the highly electronegative elements in the polymer chain.

The absorption of the TNT did not appear to occur except in two prepared films; PVF and EC and the commercial film, TED. The TNT molecule is thought to attach by means of its oxygen lone pair electrons in low concentration and by the attraction of its cloud to a surface in high concentrations.¹¹ The cloud could be attracted by the highly electronegative fluorine in the PVF and the electronegative oxygen in the hydroxyl groups as well as the oxygen atoms in the chain of EC.

CONCLUSION

From the preliminary studies, it can be concluded that the technique of preconcentrating the propellant vapors in polymers and detection by the FTIR spectrophotometer was feasible. This was supported by the ease with which MEK and nitrobenzene were detected. The subsequent detection of TNT along with DNT vapors, a frequent contaminant in TNT, verified this assumption. Compared to the highly volatile MEK and nitrobenzene, DNT and TNT have vapor pressures of 0.11 mbar and 0.14 mbar at 100°C ¹⁰, respectively, which makes preconcentration a necessity.

There are several areas that should be studied in more detail. First, the effect of vinyl acetate could be studied by preparing copolymers with both high and low density polyethylene in various proportions. Second, other polymers with highly electronegative components should be obtained and tested. Third, a study of the minimum vapor concentration needed for detection with the films should be performed with DNT and/or TNT. Fourth, polymers that function favorably should be tried with other common propellants. Finally, various plastiziers could be added to polyvinyl chloride (PVC) to test if the doping of the nonabsorptive polymer could effectively change its properties.

APPENDIX A
FTIR SCANNING CONDITIONS

STUDY	VAPOR CHAMBER	DETECTOR	NO. OF SCANS	RESOLUTION Cm-1	RANGE Cm-1	NEW BACKGROUND
Absorption MEK	Jar	TGS	1	4	4000-450	each day
Desorption MEK	Jar	TGS	1	4	4000-450	every two scans
Absorption Nitrobenzene Film	Jar	TGS	1	4	4000-450	between scans
Absorption Nitrobenzene Prepared Film	Jar	MET	6	1	2000-700	each scan
Absorption Nitrobenzene Prepared Film	Tube	TGS	3	1	2000-700	3 times/ day
Desorption Nitrobenzene	Jar	MCT	6	1	2000-700	each scan
Absorption DNT Commercial Films	Jar	MCT	6	1	2000-700	each scan
Absorption DNT Prepared Films	Jar	MCT	6	1	2000-700	each scan
Absorption DNT on EC and TED	Tube	TGS	3	1	2000-700	3 times/ day
Absorption TNT Commercial Films	Jar	MCT	6	6	2000-700	each scan
Absorption TNT Prepared Films	Jar	MCT	6	1	2000-700	each scan
Absorption TNT on EC and TED	Tube	TGS	3	1	2000-700	3 times/ day

APPENDIX B
COMMERCIAL POLYMER FILMS

Name	Label Thickness ^a	Measured Thickness ^a	Chemical Compounds	Source
Copolymer A	-	.0011	Polyethylene-vinyl acetate copolymer	Grocery
Ethyl cellulose	-	.0084	Ethyl cellulose	Grocery
Glad Cling Wrap	.0005	.0004	Polyethylene	Grocery
Glad Micro Wrap	-	.001	Polyethylene	Grocery
Glad Sandwich Bag	.00115	.0009	Polyethylene	Grocery
Handi Wrap	.00052	.0005	Polyethylene	Grocery
Large Bag	-	.0024	Polyethylene	Found
Large Bag B	-	.003	Polyethylene	Found
Pretzel Bag	-	.0029	Polyethylene-vinyl acetate copolymer	Found
Safeway Cling Wrap	.00005	.0004	Polyethylene	Grocery
Safeway Food Storage Bag	.00101	.0007	Polyethylene	Grocery
Safeway Plastic Wrap	.0005	.0004	Polyethylene	Grocery
Safeway Sandwich Bag	.0007	.0007	Polyethylene	Grocery
Safeway Storage Bag	.00175	.0018	Polyethylene	Grocery
Saran Wrap	-	.0004	Poly(vinylidene chloride) Resin	Grocery
Tedlar	-	.002	Polyvinyl flouorocarbon	Found
Vapor Barrier	-	.0032	Polyethylene	Found
Zip Type Bag B	.003	.0032	Polyethylene	Found
Zip Type Bag Clear	.003	.0026	Polyethylene	Found
Zip Type Bag Green	.004	.0038	Polyethylene	Found
Ziplock Freezer Bag	0.0027	.0027	Polyethylene	Grocery
Ziplock Storage Bag	0.00175	.00175	Polyethylene	Grocery

^a= inches

APPENDIX C
PREPARED POLYMER FILMS

Chemical Compound	Measured Thickness	Catalog Number	Lot Number	Source
Cellulose triacetate	0.0012 in	18,100-5	02106LM	Aldrich *
Ethyl cellulose	0.0014 - 0.0095 in	24,749-9	02420DT	Aldrich *
Poly(acrylonitrile)	0.0012 - 0.0030 in	18,131-5	04029LJ	Aldrich *
Polycarbonate	0.0045 in	18,162-5	01811CT	Aldrich *
Poly(methyl acrylate)	0.0030 in	18,221-4	01754JT	Aldrich *
Poly(meth acrylate)	0.0010 - 0.0030 in	18,224-9	3821KK	Aldrich *
Polystyrene	0.0033 in	18,242-7	04828MT	Aldrich *
Polyvinyl chloride High molecular weight	0.0012 - 0.0021 in	18,956-1	03350MV	Aldrich *
Polyvinyl chloride Low molecular weight	0.0012 - 0.0050 in	18,958-8	03728CV	Aldrich *
Poly(vinylidene fluoride)	0.0002 - 0.0018 in	18,270-2	03971TV	Aldrich *

* Aldrich Chemical Company
1001 West Saint Paul Avenue
Milwaukee, WI 53233

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